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(54) OPTICAL RECORDING COMPOSITION, FILM AND METHOD

(57)Abstract:
PURPOSE: To obtain a volume-phase hologram exhibiting high diffraction efficiency and having excellent environmental resistance and durability by using an inorg. network obtained from an organometallic comp. soln. by the sol-gel method.
CONSTITUTION: A photopolymerizable monomer or oligomer contg. a photopolymerization initiator is added to an organometallic compd. soln. contg. solvent, water and catalyst, agitated and mixed to coat a substrate. The hydrolysis and polycondensation of the compd. proceed thereafter to form an inorg. network, and sol is converted to gel. As the drying continues, the solvent and water in the network are vaporized, and the monomer or oligomer is distributed in the network over the entire film. As a result, contraction by polymerization is reduced in the interference-fringe recording, the optical characteristic and diffraction efficiency are improved, and the environmental resistance and mechanical characteristic are improved since the network consists of an org.-inorg. composite.

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CLAIMS

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(57) [Claim(s)]
[Claim 1] (1) the film of the network of the mineral matter which has many minute free passage holes inside constituted from mineral matter which has a certain refractive index, and (2) — the mixture of the photopolymerization nature monomer or the oligomer shut up in said free passage hole, and a photopolymerization initiator — since — the film for optical recording whose polymer when it carries out the polymerization of said photopolymerization nature monomer or oligomer is a thing with the refractive index of the value from which the refractive index of said mineral matter differs.
[Claim 2] For said polymer, the refractive index of said mineral matter is film for optical recording according to claim 1 which has a different refractive index 0.01 at least. [Claim 3] Said mixture is film for optical recording according to claim 1 or 2 which contains the solvent or plasticizer for said organometallic compound further.
[Claim 4] Said mineral matter is the film for optical recording given in any 1 term of claims 1–3 which are the things containing at least one sort of oxide chosen from the group which consists of a silicon dioxide, a titanic–acid ghost, a zirconic acid ghost, and aluminum oxide. [Claim 5] (1) A photopolymerization nature monomer or oligomer, (2) photopolymerization initiator, (3) hydrolysis, and the organometallic compound in which a polycondensation is possible, It sets here including the catalyst for promoting hydrolysis of said organometallic compound. (4) — the solvent for said organometallic compound, (5) water, and (6) — said organometallic compound The constituent for optical recording film which has a different refractive index from the refractive index which a polymer when said photopolymerization nature monomer or oligomer carries out a polymerization has hydrolysis and when a polycondensation is carried out.
[Claim 6] The aforementioned (1) – (6) component is (1) component. 10 – 80 % of the weight, (2) components 0.05 – 30 % of the weight, (3) components 5 – 90 % of the weight, (4) components 5 – 90 % of the weight, (5) components 5 – 90 % of the weight, and (6) components Constituent for optical recording according to claim 5 contained 0.05 to 30% of the weight.
[Claim 7] For said organometallic compound, the refractive index which a polymer when a polycondensation is carried out and said photopolymerization nature monomer or oligomer carries out [hydrolysis and] a polymerization has is a constituent for optical recording according to claim 5 or 6 which has a different refractive index 0.01 at least.
[Claim 8] The constituent for optical recording film according to claim 7 which contains the solvent or plasticizer for said photopolymerization nature monomer or oligomer other than the aforementioned (1) – (6) component further.
[Claim 9] The manufacture approach of the film for optical recording which is made to evaporate a solvent (4) by desiccation and is used as a solid–state–like filmy body after applying said constituent for optical recording given in any 1 term of claims 5–8 on a base material and forming hydrolysis and the film which was made to carry out a polycondensation and was gelled for said organometallic compound.
[Claim 10] The record approach of the light characterized by providing the 1st process which exposes said film for optical recording given in any 1 term of claims 1–4 to the interference fringe obtained by the radiant ray which has a coherency.
[Claim 11] The record approach of a light possessing the 2nd process which irradiates light at homogeneity at the film for optical recording, and heats the film for optical recording after that following said 1st process according to claim 10.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Industrial Application] This invention relates to the optical recording approach using the constituent for optical recording especially the constituent for optical recording which can record suitably the volume phase mold hologram which records an interference fringe by the refractive-index modulation, the film for optical recording, and this film.
[0002]
[Description of the Prior Art] Conventionally, the hologram classified into the structure to the record principle to an amplitude mold, a phase mold (refractive-index modulation mold) and a surface type, a volume mold, the direction of the illumination light at the time of playback and the diffracted light to a transparency mold (in the case of an opposite direction), a reflective mold (in the case of this direction), etc. is known. Especially as for the diffraction efficiency from which the volume phase mold is most excellent, and is obtained in optical property sides, such as diffraction efficiency, in this, it is proved that a transparency mold and a reflective mold become 100% theoretically. Therefore, not only the display hologram on which a volume phase mold hologram records an image but the application as various optical elements, such as a grating using high diffraction efficiency, optical spectral separation, a substage condenser, and a laser-beam scanning component, is considered. Since especially the volume phase mold hologram of a reflective mold has strong interferential action, its wavelength selection nature is remarkable and it is reproducible by the white light, attention is greatly attracted with the brightness of the image. Furthermore, a part of application to a HUD or laser safety goggles for the aircraft, an automobile, and cars etc. is also put in practical use using the strong wavelength selection nature.
[0003] As a hologram ingredient of a volume phase mold, the photosensitive material and dichromated gelatin (DCG) like silver salt have been used. From the sensibility of a silver salt ingredient being high, since optical properties, such as diffraction efficiency, were excellent, DCG had spread widely until now.
[0004] Now, the so-called photopolymer attracts attention in recent years as silver salt and a volume phase mold hologram ingredient which replaces DCG. Generally a photopolymer is classified into an optical bridge formation mold photopolymer and a photopolymerization mold photopolymer.
[0005] as the former example — JP,58-114029,A — said — the optical organic-functions mold polymer which has the functional group of an optical bridge formation mold is mentioned to intramoleculars, such as 58-211181. In this polymer, optical bridge formation advances according to the optical intensity distribution of an interference fringe, and an interference fringe is recorded as bridge formation distribution. Therefore, by this method, in order to acquire high diffraction efficiency, a back process takes a development.
[0006] moreover — as the latter example — JP,53-15152,A — said — 60-502125 and JP,2-3081,A — said — the combination of the so-called photopolymerization mold monomers, such as 2-3082 and 3-50588, and a binder polymer etc. is mentioned. In this case, the polymerization of a photopolymerization mold monomer advances alternatively according to the optical intensity distribution which the monomer of a photopolymerization mold contains and are formed of interference fringe exposure into a record ingredient, and an interference fringe is recorded according to presentation distribution.
[0007] In addition, the diffraction efficiency of the volume phase mold hologram of a reflective mold is defined by the degree type by Kogelnik.

Eta=tanh 2 (pin1 T/lambda BcosthetaB) (1)
For diffraction efficiency and n1, a refractive-index modulation and T are [eta /the Bragg wavelength and thetaB of thickness lambdaB] the Bragg angles here. (1) As shown in a formula, in order to enlarge diffraction efficiency, it turns out that it is required to thicken thickness or to enlarge a refractive-index modulation. However, since a bandwidth and include-angle width of face will become narrow according to increase of interferential action if thickness is thickened, it is necessary to enlarge a refractive-index modulation in the application as which the extensive bandwidth or include-angle region of playback wavelength is required. Conversely, thickness can be made smaller, if it says and a refractive-index modulation can be enlarged.
[0008]
[Problem(s) to be Solved by the Invention] However, the above-mentioned conventional constituent ingredient for volume phase mold hologram record had the trouble as shown below, respectively.
[0009] That is, the shelf life of DCG from production of sensitization material to laser exposure is very bad, and needs to adjust it each time. And complicated wet processes, such as development and fixing, are required after interference exposure, and it also has the technical problem that it cannot be said that the hologram recorded further still has enough properties, such as lightfastness and a water resisting property. These technical problems have been serious failures to the application in respect of real production of DCG.
[0010] Moreover, although the silver salt ingredient has engine performance sufficient as a hologram ingredient in respect of the sensibility, decline in that difficulty is in record of the interference fringe which has quantity resolution, i.e., the frequency between altitude, for silver corpuscular character, and transmission is a problem, and in order to make it a phase mold hologram, when a breeching is perform, it is say that a problem arises in lightfastness. And important and indispensable complicated wet processes, such as development and fixing, are required after interference exposure like DCG.
[0011] A photopolymer is being developed in recent years as what cancels the fault of the above conventional volume phase mold hologram ingredients. Generally the shelf life of a photopolymer at the time of non-laser exposure is good, and since it does not have corpuscular character, resolution is also essentially satisfactory. Moreover, it is said that lightfastness, a water resisting property, etc. can be improved by selection of various presentations, and the problem at the time of after [record] use is also being solved.
[0012] As mentioned above, in order to make an optical bridge formation mold photopolymer into a phase mold hologram, a complicated wet process is usually needed like DCG or a silver salt ingredient after interference exposure. Moreover, when enlarging especially a refractive-index difference also in a photopolymerization mold photopolymer, a wet process may be performed after interference exposure.
[0013] The polymerization of a photopolymerization mold monomer advances alternatively according to the optical intensity distribution which the so-called combination of a photopolymerization mold monomer and a binder polymer is proposed as a photopolymer which conquered the above conventional technical problems, a wet development, the lightfastness after record, a resistance to environment, etc., and the monomer of a photopolymerization mold contains in the record ingredient in this case, and are formed of interference fringe exposure, and an interference fringe is recorded according to presentation distribution. Especially, JP,3-50588,A etc. limits the fluorine content polymer of a low refractive index rather than before as a binder to the monomer of a high refractive index being conscious of acquiring high diffraction efficiency in a reflective mold phase hologram.
[0014] However, in the volume phase hologram, it is not concerned with a transparency mold and a reflective mold, but in order to desire not only the ease of carrying out of hologram records with last thing, such as the viewpoint of the application application expansion to wet process needlessness, but high thermal resistance and a resistance to environment and for a high optical property to realize it, development of radically different new hologram writing materials from the former is expected recently.
[0015] This invention conquers the technical problem of the above-mentioned conventional technique, shows an optical property, high sensitivity, etc. which were [permeability /high diffraction efficiency, high resolution, /high] excellent, and offers the constituent for optical recording which can produce the volume phase mold hologram which has the resistance to

environment excellent in coincidence, and endurance, especially the volume phase mold hologram of the reflective mold with which the application attracts attention in recent years in an easy process, and its record approach.

[0016]

[Means for Solving the Problem] the organometallic compound in which the (1) photopolymerization nature monomer or oligomer, (2) photopolymerization initiator, (3) hydrolysis, and polycondensation of this invention are possible, the solvent for said organometallic compound and (4) (5) water, and (6) — it is a constituent for optical recording including the catalyst for promoting hydrolysis of said organometallic compound.

[0017] As a photopolymerization nature monomer in this invention, the monomer containing at least one radical in which polymerizations, such as an acryloyl radical, a methacryloyl radical, a vinyl group, and an allyl group, are possible can use it for intramolecular suitably. As the example, TETORO hydronalium furfuryl acrylate, ethyl carbitol acrylate, Dicyclopentenyl oxy-ethyl acrylate, phenyl carbitol acrylate, Nonylphenoxyethyl acrylate, 2-hydroxy-3-phenoxypropylacrylate, omega-hydroxy hexanoyloxy ethyl acrylate, acryloyloxyethyl succinate, Acryloyl OKIE chill succinate, acryloyloxyethyl phthalate, Phenyl acrylate, naphthyl acrylate, TORIBUROMO phenyl acrylate, Phenoxy ethyl acrylate, TORIBUROMO phenoxy ethyl acrylate, Benzyl acrylate, p-BUROMO benzyl acrylate, 2, and 2-screw (4-meta-chestnut ROKISHI ethoxy -3, 5-dibromo phenyl) propane, Isobornyl acrylate, 2-ethylhexyl acrylate, laurylacrylate, The methacrylate corresponding to these monofunctional nature acrylate to monofunctional nature acrylate lists, such as 2, 2, 3, and 3-tetrafluoropropylacrylate; 1,6-hexanediol diacrylate, Butanediol diacrylate, EO conversion tetrabromobisphenol A diacrylate, A pentaerythritol thoria chestnut rate, trimethylolpropane triacrylate, The methacrylate corresponding to these polyfunctional acrylate to polyfunctional acrylate lists, such as bisphenol A diacrylate; Styrene, p-chloro styrene, a divinylbenzene, vinyl acetate, acrylonitrile, Vinyl compound; and diethylene-glycol bisallyl carbonate, such as N-vinyl pyrrolidone, vinyl naphthalene, and N-vinylcarbazole, Allyl compounds, such as triallyl isocyanurate, JIARIRI DIN pentaerythritol, diallyl phthalate, and diallyl isophthalate, etc. are mentioned (mixture is included).

[0018] Although the methacrylate corresponding to polyfunctional oligo acrylate and these acrylate, such as urethane acrylate oligomer, epoxy acrylate oligomer, ester acrylate oligomer, polyol polyacrylate, denaturation polyol polyacrylate, and polyacrylate of an isocyanuric acid frame, is mentioned besides the oligomer of the above-mentioned photopolymerization nature monomer as an example of the photopolymerization nature oligomer used by this invention (mixture is included), it is not limited to this.

[0019] What is generated by the addition reaction of the poly isocyanate, 2-hydroxyalkyl (meta) acrylate, and polyol as polyurethane acrylate oligomer is illustrated. Here, as poly isocyanate, toluene diisocyanate, isophorone diisocyanate, trimethyl hexamethylene di-isocyanate, hexamethylene di-isocyanate, etc. are mentioned. Moreover, as polyol, polyether polyols, such as a polyethylene glycol, a polypropylene glycol, and a polytetramethylene glycol, polyester polyol, polycarbonate polyol, polysiloxane polyol, etc. are mentioned.

[0020] As an organometallic compound in which the hydrolysis and the polycondensation which are used by this invention are possible, the thing containing at least one sort in an organic silicon compound, an organic titanium compound, an organic zirconium compound, and an organoaluminium compound is desirable, and the metal alkoxide which has especially an alkoxyl group is desirable. Specifically, methoxides, such as silicon, titanium, a zirconium, and aluminum, ethoxide, propoxide, butoxide, etc. are used by the simple substance or the mixture. Organoaluminium compounds, such as organic zirconium compound; aluminum ethoxide, such as organic titanium compound; zirconium methoxides, such as organic silicon compound; titanium isopropoxide, such as a tetra-ethoxy silane, a tetramethoxy silane, and tetra-butoxysilane, and titanium butoxide, and zirconium butoxide, and aluminum butoxide, etc. are mentioned as the example. Moreover, you may embellish with the compound which has the functional group in which other organic monomers and a polymerization are possible like the compound which has the organic section in side chains, such as dimethylsiloxane, an amino silane, and poly dimethylsiloxane of a silanol end, or vinylsilane, an acrylic silane, and an epoxy silane organically.

[0021] In addition, metal inorganic compounds, such as carboxylate, such as metal acetylacetonate, acetate, and an oxalate, and a nitrate, a chloride, and an oxysalt ghost, may be used besides the above-mentioned metal alkoxide.

[0022] An inorganic network is formed from a sol and the above-mentioned organometallic compound serves as gel as it hydrolyzes in a solution and a polycondensation progresses. If heating-at-high-temperature processing of this gel is carried out, a metallic-oxide solid-state can be created.

[0023] Moreover, the catalyst for promoting a solvent, water, and said hydrolysis for the organometallic compound in which the hydrolysis and the polycondensation which are used by this invention are possible, hydrolysis and in order to carry out a polycondensation is required. As a solvent which should dissolve this organic metal compound, alcohols, such as a methanol, ethanol, propanol, and a butanol, are the most desirable. Moreover, as the above-mentioned catalyst, bases, such as acids, such as a hydrochloric acid, an acetic acid, a sulfuric acid, and a nitric acid, and ammonia, are used.

[0024] The above-mentioned organometallic compound's differing from hydrolysis and the refractive index obtained by carrying out a condensation reaction and the difference of this refractive index have so desirable that it is large the refractive index of a polymer when it carries out the polymerization of an above-mentioned photopolymerization nature monomer or oligomer. It is required for both difference to be at least 0.01 preferably, and it is necessary to choose the combination of a photopolymerization nature monomer or oligomer, and an organometallic compound so that the difference of such a refractive index may arise. The difference of this refractive index is big, for example, if 0.03 or more combination is chosen, a big refractive-index modulation important for a volume phase mold hologram can be obtained. If it follows, for example, the inorganic network is formed from SiO2 of a low refractive index, the monomer of a high refractive index will be used as a photopolymerization nature monomer. It is important to, use the monomer of a low refractive index relatively as a photopolymerization nature monomer on the other hand, if formed from TiO2 of a high refractive index. As a concrete example of the desirable above-mentioned combination, 2-hydroxy-3-phenoxypropylacrylate (the refractive index of the polymer when carrying out a polymerization = 1.555), a tetra-ethoxy silane (hydrolysis, the refractive index obtained by carrying out a condensation reaction and finally carrying out densification = 1.46) and trimethylolpropane triacrylate (refractive index = 1.519), titanium propoxide (refractive index = 2.40), etc. are mentioned.

[0025] In order to carry out the polymerization of an above-mentioned photopolymerization nature monomer or oligomer efficiently, it is necessary to add a photopolymerization initiator to this. The compound shown below as a photopolymerization initiator of this invention is mentioned. For example, 2, 3-bornane dione (camphor quinone) 2, 2, 5, and 5, - tetramethyl tetrahydro - Annular cis—alpha-dicarbonyl compounds, such as 3 and 4-furan acid (imidazoletrione), Benzophenones, such as 3, 3', 4, and a 4'-tetrapod-(tert-butyl peroxide carbonyl) benzophenone, Diacetyl, benzyl, a MIHIRAZU ketone, a diethoxy acetophenone, Ketones, such as 2-hydroxy 2-methylpropiohenone and 1-hydroxy cyclohexyl phenyl ketone Peroxides, such as benzoyl peroxide and di-t-butyl peroxide, Aromatic carboxylic acid, such as azo compounds, such as allyl compound diazonium salt, and N-phenylglycine, Xanthenes, such as 2-chloro thioxan ton, 2, and 4-diethyl thioxan ton Diaryl iodonium salt, triaryl sulfonium salt, triphenyl alkyl way acid chloride, An iron allene complex, bis-imidazole derivatives, the Pori halogenated compound, phenyl iso oxazolone, benzoin ethyl ether, benzyl dimethyl ketal, etc. are mentioned (mixture is included). Furthermore, amines, thiols, p-toluenesulfonic acid, etc. are mentioned as an assistant.

[0026] The constituent for optical recording of this invention expresses with a principal component. The sum total of a photopolymerization nature monomer or oligomer 10 - 80 % of the weight, a photopolymerization initiator 0.05 - 30 % of the weight, said organometallic compound The solvent for 5 - 90 % of the weight, and said organometallic compound 5 - 90 % of the weight, water 5 - 90 % of the weight, and said catalyst It is desirable to contain 0.05 - 30 % of the weight. The above-mentioned photopolymerization nature monomer or diffraction efficiency with the sum total of oligomer expensive at less than 10 % of the weight or 80 % of the weight or more becomes is hard to be acquired. If the above-mentioned organometallic compound exceeds less than 5 % of the weight or 90 % of the weight similarly, high diffraction efficiency will not be acquired.

[0027] A photosensitizer can be contained and it can make 0.01 - 10 % of the weight contain [constituent /this] a plasticizer 0.01 to 10% of the weight if needed, respectively.

[0028] The photopolymerization nature monomer or oligomer to be used is a solid-state, or to have high viscosity, the solvent for dissolving it is required. However, since isopropyl alcohol is also the solvent of 2-hydroxy-3-phenoxy hexyl acrylate (solid photopolymerization nature monomer) while

being the solvent of a tetra-ethoxy silane (organometallic compound in which hydrolysis and a polycondensation are possible) when dissolving in the solvent for the organometallic compound which a photopolymerization nature monomer or oligomer described previously for example, as for the isopropyl alcohol which is a solvent for said organometallic compound, the solvent for a photopolymerization nature monomer or oligomer can be made to serve a double purpose.

[0029] Moreover, organic qualification of the inorganic network is carried out by dimethylsiloxane, the amino silane and the poly dimethylsiloxane of a silanol end, gamma-methacryloxypropyl triethoxysilane, and gamma-guru SHIJIROKISHI propyl triethoxysilane as the organometallic compound in which hydrolysis and a condensation reaction are possible, for example, a silicon system compound, and it does not matter as organic inorganic complex. That is, the brittleness which introduces an organic radical for dimethylsiloxane and poly dimethylsiloxane all over a siloxane inorganic network combining the above-mentioned hydrolysis and the organometallic compound in which a polycondensation is possible, for example, a tetra-ethoxy silane, among the above-mentioned compounds, and is made to give flexibility, and the optical recording film has can also be softened.

[0030] A plasticizer can be added to the constituent for optical recording of this invention. A plasticizer is for giving plasticity to the photopolymerization mold monomer in the constituent for optical recording (or oligomer), and can mention triethylene glycol dicaprylate, triethylene glycol diacetate, triethylene glycol dipropionate, a glyceryl TORIBUCHI rate, tetraethylene glycol JIHEPUTANOETO, a diethyl reed peat, diethyl sebacate, tributyl phosphate, etc. as an example of a plasticizer.

[0031] Furthermore, a sensitizer like coloring matter can be added to the constituent for optical recording of this invention. Although the compound shown below as coloring matter used is mentioned, it is not limited to this. For example, it is the compound which has extinction in light (mixture is included) regions, such as a methylene blue, an acridine orange, thioflavine, a keto coumarin, Erythrosine C, eosine Y, merocyanine, a phthalocyanine, and a porphyrin.

[0032] Moreover, it is very useful when adding the additive of a leveling agent and others in addition to the above-mentioned component also actually provides as a film for optical recording to the constituent for optical recording of this invention.

[0033] Next, the principle of this invention is described.

[0034] The photopolymerization nature monomer or oligomer which contained additives, such as a photosensitizer and a plasticizer, in the constant-rate **** organometallic compound solution a photopolymerization initiator and if needed is added, the acid or base which is a solvent, water, and a catalyst is stirred, and it mixes. Coating of the solution mixed by homogeneity is carried out by various approaches on a substrate, and a filmy body is obtained. Although it is the filmy body which consists of a viscous liquid in this phase, hydrolysis of an organometallic compound and a polycondensation advance, an inorganic network is formed, and it changes from a sol to gel as time amount passes after coating. Furthermore, by advancing a forced drying or an air drying, volatile components contained all over the inorganic network, such as a solvent and water, evaporate, and solid-state-like the film for optical recording (filmy body) is obtained as a result. In this process, although the pore (opening) which was mutually open for free passage is formed in an inorganic network, since liquid-like a photopolymerization nature monomer or oligomer exists in coincidence in this invention, pore is filled one by one by these and contraction of the big network which is usually generated in a sol gel process for this reason is not generated substantially. A photopolymerization nature monomer or oligomer will be distributed all over the inorganic network currently finally formed over the whole filmy body. Although the specific surface area of the film to which a uniform light was irradiated, was photopolymerized on the film of this condition, and the polymerization of a monomer or the oligomer was carried out was measured with the BET adsorption method, specific surface area was zero substantially. In addition, although close [of a photopolymerization nature monomer or an oligomer monomer] made the film similarly using the constituent which is not and measured this as an example of a comparison, since it was 420m2/g in this case, it is shown that most pores formed during the sol gel reaction substantially [the inorganic network made by this invention] are altogether filled with a photopolymerization nature monomer or oligomer.

[0035] Moreover, in this invention, if it sets up so that the field of the organic part which fills the above-mentioned pore may not become larger than wavelength order, even if both refractive indexes differ, there will be little dispersion and it will serve as transparence substantially.

[0036] Although a photopolymerization nature monomer or oligomer is held all over the inorganic network formed in the whole film in the manufactured original film for optical recording at homogeneity, in order to perform optical recording, a polymerization is alternatively started by the optical intensity distribution inside the film for optical recording by exposure of the interference fringe formed of two-beam-interference exposure of laser etc. That is, since a polymerization starts, it swerves and takes in a part with strong optical reinforcement and a monomer is consumed, a monomer is supplied to a part with strong optical reinforcement from a part with the optical weak reinforcement which adjoined, and a polymerization is promoted further. In this case, a part of inorganic network where optical reinforcement existed in the strong part from the first It extrudes with the polymer to which the volume became large by the monomer to which optical reinforcement was supplied from the weak part. The polymer rich field as for which optical reinforcement will move or shift to a weak adjacent part, and the photopolymerization nature monomer (or oligomer) whose optical reinforcement is finally a strong part carried out the polymerization, It is relatively classified into an inorganic network rich field, and it is thought [whose it is a part with optical weak reinforcement conversely] that a big presentation difference arises between both the field. As the difference of the refractive index Np of a polymer and the refractive index Nm (refractive index which the mineral matter which hydrolyzed and carried out the polycondensation and was able to do said organometallic compound has) of an inorganic network in which the photopolymerization nature monomer (or oligomer) carried out the polymerization at this time is large, it becomes more possible to balance a presentation difference and to give a big refractive-index difference.

[0037] The record ingredient for light in this invention has the advantage which is expressed below compared with the photopolymerization mold photopolymer type thing using the thermoplastic polymer binder of the conventional solvent fusibility.

[0038] In the first place, increase of a refractive-index modulation is mentioned. In the case of an organic binder, a limitation is in the refractive index of a polymer, and 1.6 sets are considered to actually consider the upper service condition also with whether it is a limitation. On the other hand, since very high refractive indexes, such as 2.2-2.4, are also obtained when densification is carried out using a titania, a zirconia, etc. in the case of an inorganic network, the material for optical recording which has a still bigger refractive-index difference is also obtained. Of course, the silica of a refractive index 1.46 and the combination of a high refractive-index monomer are conversely sufficient.

[0039] Since the film for optical recording or optical recording film of this invention finally obtained has changed to the second from very micro organic inorganic complex structure, as compared with the conventional article polymer type [all], high thermal resistance, a resistance to environment, a mechanical property, etc. are acquired. Moreover, when an inorganic network is a silica, an adhesive property with a glass substrate improves by silanol association.

[0040] Since the interference fringe which has detailed spacing is recorded in case optical recording is actually carried out, it is necessary to take care that the whole exposure optical system is carried on a vibrationproofing base, and careful cautions are carried out to vibration, fluctuation of air, etc., and the film for optical recording itself does not move in process of interference fringe record.

[0041] After it applies said constituent liquefied object for optical recording on a base material as mentioned above and an organometallic compound gels hydrolysis and by carrying out a condensation reaction in this invention, a solvent etc. is made to evaporate by desiccation and it considers as a solid-state-like filmy body. Since the inorganic network is maintaining the shape of a solid-state at this time, there is no possibility that it may be displaced relatively to a base material in process of interference fringe record. Moreover, since it is a solid-state-like, the thickness which has serious effect for the optical property of record light can be specified correctly, and the upper handling nature also actually improves.

[0042] In this invention, by using an inorganic network, the curing shrinkage at the time of interference fringe record of an optical ingredient can be reduced as much as possible, and the effectiveness that an interference fringe is faithfully recordable is done so. That is, fundamentally, since the constituent for optical recording of this invention belongs to the ingredient of a photopolymerization mold, it is surely accompanied by curing shrinkage before and after interference fringe record. If this curing shrinkage is large, it is difficult to record an interference fringe faithfully too, and since the serious bad influence for the optical property of light especially

diffraction efficiency, playback wavelength, etc. is done, it is necessary to make the rate of curing shrinkage small as much as possible. Since record of a very fine interference fringe is especially required in the volume phase mold optical recording of a reflective mold as compared with record of a transparency mold, contraction of the record ingredient under exposure etc. must be avoided as much as possible. If the refractive-index difference made by the alternative polymerization of the above-mentioned photopolymerization nature monomer (or oligomer) is not faithfully recorded to the fine interference fringe, either, half-value width of diffraction efficiency and playback wavelength etc. cannot be obtained near the theoretical value by the phase mold hologram, especially the reflective mold hologram.

[0043] In this invention, by using the inorganic network obtained from the organometallic compound solution using the sol gel process, the curing shrinkage at the time of interference fringe record of a hologram ingredient can be reduced as much as possible like the photopolymer for hologram record using a binder, and an interference fringe can be recorded faithfully. Therefore, it became possible to obtain mostly the half-value width of the important optical property of a hologram, diffraction efficiency, and playback wavelength etc. as a theoretical value. This effectiveness brings about remarkable effectiveness especially in the reflective mold hologram of which very fine interference fringe record is required.

[0044] It is desirable that a solvent remains to some extent in hologram record film. If a solvent disappears completely, the diffraction efficiency of the optical recording film obtained by carrying out laser exposure will become quite low. It is thought that this reason is because the viscosity of the monomer by which supply migration of the optical reinforcement should be carried out from a weak part to a strong part becomes high and it becomes inadequate that supplying the optical reinforcement which the polymerization was alternatively started by the optical intensity distribution inside the film for optical recording, and adjoined. Therefore, existence of a certain amount of [such phase separation] solvent to a request ********** sake is required. However, if the plasticizer of a high-boiling point is beforehand added in the constituent for optical recording, the effectiveness like lubricant is shown to phase separation like a solvent, and even if it performs reduced pressure drying to which a solvent disappears nearly completely, since a plasticizer remains, the optical recording film which has high diffraction efficiency is obtained.

[0045] Next, how to record light using the constituent for optical recording of this invention is explained. In order to prepare material for optical recording, photopolymerization nature oligomer, a monomer, a photopolymerization initiator, and a photosensitizer are dissolved into the acid used as a sol gel start solution, i.e., water, a solvent, and a catalyst, and the organometallic compound solution containing a base, but if required, the solvent (such mixture is included) of a methanol, ethanol, isopropanol, toluene, dioxane, chloroform, dichloromethane, a methylene chloride, a tetrahydrofuran, and others will be used, for example. The amount of these solvents used is usually the 10 - 1000 weight section to the principal component 100 weight section (except for a solvent) of the constituent for optical recording.

[0046] Then, after adding the constituent for optical recording of other this inventions by the above presentation ratios, coating is performed for this liquefied object using the various methods of application on smooth front faces, such as a glass plate and a resin film. As the coating approach, various approaches, such as an approach which used the doctor blade and the applicator in addition to the spin coat, the DIP coat, the flow coat (curtain coat), etc., are applicable.

[0047] The evaporation [solvent /which was used when required and dissolving further a condition, the solvent contained in the sol gel start solution, photopolymerization nature oligomer, or a monomer under a reduced pressure condition] out of the paint film of the above-mentioned sensitive material then, a room temperature or warming — Removal obtains solid-state-like the film for optical recording with which photopolymerization nature oligomer, the monomer, the photopolymerization initiator, the photosensitizer, etc. were incorporated all over the inorganic network formed by the sol gel process in the condition of having been covered on the smooth front face. The thickness after desiccation of the film film for optical recording is usually 1-50 micrometers. Then, a transparent resin film or a transparent glass plate is covered on the front face of the obtained film for optical recording using a suitable approach to the radiant ray which has the coherency exposed at degree process. This is for preventing adhesion of dust, a foreign matter, etc., in order that this constituent may prevent the polymerization inhibitory action by oxygen, since a polymerization advances by the radical polymerization.

[0048] Next, the interference fringe obtained by the radiant ray which has a coherency is made to

expose the film for optical recording with which the above was covered. The well-known approach that generally the laser light source is used for this process (the 1st process) as the coherent light source is used. As the approach of interference exposure, it can carry out using the conventional optical exposure optical system. Usually, this approach is called the two-beam-interference exposing method. The laser beam oscillated from a laser oscillation machine is divided into two parallel light or the diffused light using a beam splitter, a beam expander, a collimator lens, etc. And incidence is carried out to material for optical recording by making the flux of light of one of these into a reference beam. The flux of light of another side is irradiated by the body when recording for example, a body image, and incidence is carried out to material for optical recording by making the reflected light from there into body light. At this time, a reference beam and body light form an interference fringe, and that interference fringe is recorded on a hologram record ingredient. In addition, when it has arranged so that both flux of lights may be irradiated from the same direction, a transparency mold hologram is recorded, and when it has arranged so that it may irradiate from an opposite direction, a reflective mold hologram is recorded. Although the irradiation time of the radiant ray which has a coherency for making an interference fringe expose changes with the reinforcement of the radiant ray, record area, and others, it is usually 0.1 seconds - 30 minutes, and it is exposed so that total light exposure may become 0.1 - 1000 mJ/cm2.

[0049] In this invention, a hologram is recordable only at the 1st process which exposes the above-mentioned constituent for hologram record to the interference fringe obtained by the radiant ray which has a coherency. However, the polymerization of the photopolymerization nature oligomer of the non-polymerization which remains in this record ingredient for light at the 1st process of the above, next the 1st process, and a monomer is completed, and it is desirable to pass through the 2nd process which deactivates photosensitizers, such as an unreacted photopolymerization initiator and coloring matter.

[0050] This process can be performed by performing the uniform optical exposure which contains a polymerization or the wavelength which can react to the constituent for optical recording after interference exposure. Since especially in the case of a reflective mold hologram the diffraction efficiency of a record hologram increases so that clearly from the theoretical formula of the aforementioned (1) formula, since the polymerization of the non-polymerization oligomer in an optical ingredient and a monomer is promoted by this homogeneity light exposure and a refractive-index difference increases as compared with the case of only the 1st process by it, it is desirable. Furthermore, according to the 2nd process, a photopolymerization initiator and a photosensitizer can also be made inactive and, thereby, the endurance of a recording film, i.e., thermal resistance, moisture resistance, etc. improve. The optical exposure of this 2nd process is performed so that total light exposure may usually become about ten to 10000 mJ/cm2.

[0051] moreover, the above instead of the optical exposure with the above uniform as the 2nd process — subsequently heat-treatment more than 60-degreeC may be carried out to a uniform optical exposure to the constituent film for optical recording after interference exposure. Since phase separation was promoted, the polymerization of the non-polymerization oligomer in material for optical recording and a monomer was completed, the refractive-index difference increased upwards by this heat-treatment, and it is fixed and a solvent is evaporated, as mentioned above, the diffraction efficiency of record light increases further, and the endurance of a recording film, i.e., thermal resistance, its moisture resistance, etc. improve. The above-mentioned heating conditions are usually 1 minute - 4 hours at 60-200 degrees C.

[0052]

[Effect of the Invention] If the record approach of this invention is applied to the constituent for hologram record by this invention, the complicated wet process after interference exposure is not needed, but the volume phase mold hologram which shows the optical property which was [permeability /high diffraction efficiency, high resolution, /high] excellent in low thickness with simple dry-type after treatment and the outstanding lightfastness, thermal resistance, a resistance to environment, etc. can be obtained. In case especially the constituent for optical recording and its record approach of this invention record the volume phase mold hologram of the reflective mold with which the application attracts attention in recent years, they are useful.

[0053] Furthermore, since a refractive-index modulation can be enlarged according to this invention, the extensive bandwidth of high diffraction efficiency and playback wavelength is realizable for coincidence. And if it expands by using an organic solvent for the interlayer spacing of an interference fringe, and making record film swell after record and is made ununiformity

structure, since the formation of long wavelength of playback wavelength and band width expansion of playback wavelength are possible, it is useful also as an aperture for construction and cars as heat ray reflective film.

[0054]

[Example] Hereafter, although the example of this invention is given and explained, this invention is not limited to these examples.

[0055] In addition, a transparency mold and reflective mold Jolo Fulham (diffraction grating) were produced using the exposure optical system it is indicated to drawing 1 and drawing 2 that can grasp the potential of an ingredient simple in the example shown below.

[0056] Drawing 1 shows the optical system which records a transparency mold hologram (diffraction grating). Ar ion laser 1 — comprehensive output; — they are 4W and wavelength;514.5nm. For a spatial filter and 4, as for beam-splitter, 6, and 6', a collimator lens and 5 are [2 /a shutter and 3 /a mirror and 7] record ingredients. In this case, the spatial frequency (fringe spacing) of the interference fringe generated changes with the incident angles theta of the flux of light over the record material 7.

[0057] Moreover, drawing 2 shows the optical system which records a reflective mold hologram (diffraction grating). In this case, a mirror 9 is installed in the flesh side of 7 of a hologram record ingredient, and the interference fringe formed of the parallel flux of light acquired with the collimator lens 4 and the reflected light reflected by the mirror is recorded. At this time, refractive-index adjustment liquid (xylene) 8 was used between substrate glass and the mirror installed in a flesh side.

<Explanation of the compound shown below>TEOS : Tetra-ethoxy silane PDMS : Poly dimethylsiloxane THF : Tetrahydrofuran i-PA : Isopropyl alcohol HCl : 12-N hydrochloric-acid Ti (PO)4: — titanic-acid isopropyl M5700 2-hydroxy-3-phenoxypropylacrylate TMPTA: — trimethylolpropane triacrylate TMPTA-EO6:TMPTA ethyleneoxide 6 unit addition product BPhA : TORIBUROMO phenyl acrylate POA : Phenoxy ethyl acrylate BTTB : 3, 3', 4, 4'-tetrapod - (tert-butyl peroxide carbonyl) Benzophenone (the Nippon Oil & Fats make, 50% of purity)
KCD : 3 and 3'-carbonyl screw (7-diethylamino coumarin)
(Made in a Japanese sensitizing dye lab) an example 1 — the organometallic compound solution was first prepared on condition that the following.

<A solution 1>——— TEOS : 45gPDMS(s): 5gTHF(s) 10 cci-PA 15 cc ——— <A solution 2>——— i-PA 20ccH(s)2O 7.8ccHCl3.6cc ——— After preparing and stirring a solution 1 and a solution 2 separately, stirring the solution 2 which is the catalyst of a sol gel reaction (hydrolysis, polycondensation) in a solution 1, it was dropped and, in addition, the uniform solution was obtained. Then, this solution was ****(ed) for 30 minutes at 80 degrees C, and the uniform organometallic compound solution (start solution) was obtained.

[0058] next, the photopolymerization initiator of the following presentations and the solution 3 of the photopolymerization monomer constituent containing coloring matter — the above-mentioned start solution — receiving — a weight ratio — 20 — it introduced 25 or 33% of the weight, and three kinds of hologram record constituents of a uniform solution condition were obtained after stirring mixing. In addition, after dissolving in the methylene chloride and the methanol, BTTB and keto coumarin system coloring matter were beforehand introduced into the photopolymerization monomer, and had become a uniform monomer solution.

<A solution 3>———
TMPTA-EO6 4.75gTMPTA(s) 0.25gBTTB(s) 1.00g keto coumarin system coloring matter 0.05g methylene chloride /methanol (=95/5 % of the weight) 2.00g ——— The applicator was used and coated with the bottom of the lamp for dark rooms on the 300x150x2mm glass substrate after mixing, three kinds of constituents finally obtained were put for about 10 hours, the solvent (a methylene chloride and methanol) was fully volatilized, and the sensitization layer whose thickness is about 10 micrometers was obtained. Then, the covering film of polyethylene terephthalate with a thickness of 100 micrometers was made to adhere on the above-mentioned sensitization layer, it cut in magnitude of 60x60mm, and the sensitization material (optical recording film) which consists of a layered product of a glass substrate-sensitization layer-polyethylene terephthalate film was obtained.

[0059] Next, the 514.5nm light oscillated from Ar ion laser 1 in optical system as shown in drawing

1 was divided into the parallel light of the 2 flux of lights by the collimator lens 4 and the beam splitter 5, and to the above-mentioned sensitization material (layered product of a glass substrate-sensitization layer-polyethylene terephthalate film), at the include angle theta, incidence was carried out and it exposed. In addition, the values of an include angle theta were 5 degrees, 14 degrees, and 42 degrees, respectively.

[0060] Heat-treatment was performed for sensitization material at complete exposure and 100 degrees C from the distance of 3cm after interference exposure for 2 hours for about 20 minutes using the fluorescent lamp of 30W, the polymerization of non-polymerization oligomer and a monomer was completed, and it fixed.

[0061] When the transparency mold hologram (diffraction grating) was recorded on three kinds of record ingredients of each using the interference fringe which has 200 and 500 or 1300 spatial frequency/mm as mentioned above, in any case, it was recorded good. inside — a monomer constituent — 25wt(s)% — by the introduced system, the bright diffracted light was observed especially. In addition, presentation [which] is 30-50 mJ/cm2, and, as for exposure sensibility, showed high sensibility.

[0062] When carrying out incidence of the laser beam to this transparency mold hologram, in the case of the transparency mold hologram which has 1000 spatial frequency/mm the diffracted light is observed as theoretical and especially the Bragg diffraction is shown clearly for each hologram, the bright primary diffracted light was observed. The diffraction efficiency at this time was about 35% about the system which introduced the 25wt% monomer.

[0063] the photopolymerization monomer constituent and solution 4 which contain the photopolymerization initiator of the following presentations, and coloring matter to the start solution which consists of an organometallic compound solution shown in example 2 example 1 — the above-mentioned start solution — receiving — a weight ratio — 20, 25, and 33wt% — it introduced and three kinds of hologram record constituents of a uniform solution condition were obtained after stirring mixing.

<A solution 4>——————————————— M5700 4.75gTMPTA(s) 0.25gBTTB(s) (the Nippon Oil & Fats make, 50% of purity) 1.00g keto coumarin system coloring matter 0.05g methylene chloride /methanol =95/5wt% 2.00g ——————————————— The constituent finally obtained is produced as a sensitive film of about 8-micrometer thickness like an example 1. When the transparency mold hologram (diffraction grating) which has 200 and 500 or 1000 spatial frequency/mm was recorded into three kinds of record ingredients at each, in any case, it was recorded good like the case of an example 1.

[0064] When carrying out incidence of the laser beam to this transparency mold hologram, the diffracted light with each hologram bright as theoretical was observed, and the primary diffracted light also with mm very bright in 1000 [/] especially the Bragg diffraction is shown clearly in the case of a transparency mold hologram was observed.

[0065] Although the brightness of the diffracted light was one or more examples, since the refractive-index modulation with it was obtained, this is considered. [the higher therefore refractive index of the used photopolymerization monomer and] [bigger] In addition, even if it heat-treated the transmission grating obtained by this example at 300 degrees C for 2 hours, the function of a diffraction grating was not lost but showed high thermal resistance. As an example of a comparison, although the hologram of a total organic presentation was also processed to coincidence, the function of a diffraction grating had disappeared completely [here].

[0066] By this example, record of a reflective mold hologram was tried using the recording film obtained in the example 3 example 2. The exposure approach is as being shown in drawing 2 . That is, the mirror 9 was installed in the flesh side of the above-mentioned sensitization material (layered product of a glass substrate-sensitization layer-polyethylene terephthalate film) through refractive-index adjustment liquid (xylene) 8, and the interference fringe formed of the parallel flux of light acquired with the collimator lens 4 and the reflected light reflected by the mirror was recorded.

[0067] After the above-mentioned interference exposure, although complete exposure and heat-treatment were performed, diffraction efficiency increased for every process and a maximum of 43% of value was acquired after 200-degree-C heat-treatment. This result is shown in the following tables. In addition, the exposure sensibility required at this time was also 30-50 mJ/cm2 and high sensibility.

——————————— Each process Diffraction efficiency (%)

---------- After interference exposure After 10.0 complete exposure 21.1 heat-treatment 100 degreeC-2hr 25.9200 degreeC-2hr 43.0 ---------- The organometallic compound solution was adjusted on four or less-example conditions.
<A solution 5>---------- Ti(OPr) 4:20 gi-PA 20 cc<solution 6>i-PA 40ccH(s)2O 0.5ccHCl(s) Two cc ----------
---- After stirring a solution 5 and a solution 6 separately, stirring the solution 6 which is the catalyst of a sol gel reaction (hydrolysis, polycondensation) in a solution 5, it was dropped and, in addition, the uniform solution was obtained. Since the alkoxide of titanium tended [very] to have received hydrolysis, the start solution was obtained without ****(ing) in this case.
[0068] The photopolymerization monomer constituent containing the photopolymerization initiator of the following presentations and coloring matter was introduced into this start solution 1/2 by the weight ratio to the start solution. The uniform solution which dissolved completely was obtained after stirring mixing. In addition, after dissolving in the methylene chloride and the methanol, BTTB and keto coumarin system coloring matter were beforehand introduced into the photopolymerization monomer, and had become a uniform monomer solution.
---------- M5700 3gBTTB(s) (Nippon Oil & Fats) 0.4g keto coumarin system coloring matter 0.01g methylene chloride 1.5g methanol 0.5g ----------
---------- The constituent finally obtained was exposed by the same approach as an example 1, and the transmission grating was produced. In this case, in the case of 1000 spatial frequency/mm, it is after complete exposure, about 35% of diffraction efficiency was acquired, and about 40% of diffraction efficiency was acquired after the heat-treatment which is 100 more degrees C and 1 hour.

[Translation done.]

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1.This document has been translated by computer. So the translation may not reflect the original precisely.
2.**** shows the word which can not be translated.
3.In the drawings, any words are not translated.

DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]
[Drawing 1] It is an example of optical system used as an example of this invention when recording a transparency mold hologram (diffraction grating).
[Drawing 2] It is an example of optical system used as other examples of this invention when recording a reflective mold hologram (diffraction grating).
[Description of Notations]
1 .. a laser oscillation machine,
2 .. a shutter,
3 .. a special filter,
4 .. a collimator lens,
5 .. a beam splitter,
7 .. a hologram record ingredient,
8 .. refractive-index adjustment liquid (xylene),
9 .. a mirror

[Translation done.]